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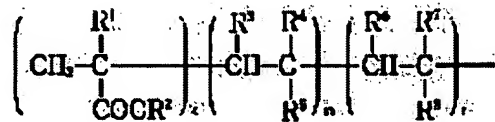
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(54) ANTIREFLECTION FILM MATERIAL AND PATTERN FORMING METHOD

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain an antireflection film material excellent in film forming property and capable of forming a resist pattern with high reproducibility by using a specified water-soluble fluororesin in combination with an amine salt of an F-contg. org. acid.

SOLUTION: This antireflection film material consists essentially of a water-soluble fluororesin represented by the formula and an amine salt of an F-contg. org. acid. In the formula, R1 is H or methyl, R2 is $-(CH_2)_a(CF_2)_bX$, etc., R3 is carboxyl, etc., R4 is $-CH_2COOH$, etc., R5 is $-C(=O)YR_{12}COOH$, etc., R6 is $-COONR_{13}R_{14}R_{15}R_{16}$, etc., R7 is $-CH_2COONR_{13}R_{14}R_{15}R_{16}$, etc., R8 is $-C(=O)YR_{12}SO_3NR_{13}R_{14}R_{15}R_{16}$, etc., R12 is an alkylene, each of R13-R16 is an alkyl, etc., X is H or F and Y is $-O-$ or $-NH-$.



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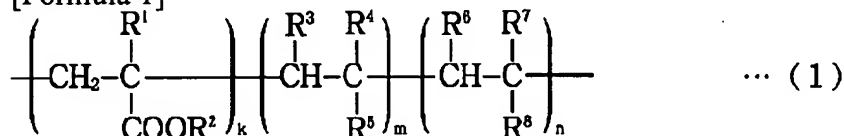
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CLAIMS

[Claim(s)]

[Claim 1] The antireflection film ingredient characterized by using as a principal component fluororesin melttable in the water shown by the following general formula (1), and the amine salt of a fluorine content organic acid in the antireflection film which is formed on the photoresist layer formed on the substrate, and forms the transparent antireflection film removed with a solvent after exposure.

[Formula 1]



however, the inside R1 of a formula -- a hydrogen atom or a methyl group, and R2 -(CH2) a(CF2) bX or -CR nine R10R11, and R3 -- a hydrogen atom -- A methyl group or a carboxyl group, and R4 A hydrogen atom, a methyl group, a carboxyl group, or -CH2COOH, R5 A carboxyl group, a sulfonic group, -C(=O) YR12COOH, or -C(=O) YR12SO3H, A hydrogen atom, a methyl group or -COONR 13R14R15R16, and R7 R6 A hydrogen atom, A methyl group, - COONR 13R14R15R16 -CH2COONR 13R14R15R16 and R8 Or -COONR 13R14R15R16, -SO3NR 13R14R15R16, -C(=O) YR12COONR 13R14R15R16, or -C(=O) YR12SO3NR 13R14R15R16, R9-R11 are a hydrogen atom, a fluorine atom, or a trifluoromethyl radical. As for a fluorine atom or a trifluoromethyl radical, and R12, the straight chain of carbon numbers 1-6 or the alkylene group of the letter of branching, and R13-R16 are [at least two of R9-R11] the alkyl group or alkyl group fluoride of the straight chain of a hydrogen atom and carbon numbers 1-8, or the letter of branching. Moreover, X is a hydrogen atom or a fluorine atom, Y is -O- or -NH-, a is [the integer of 1-8, and k and the ratio of (m+n) of 0-2b] k:(m+n) =1:9-9:1, and k is a positive number, m and n0, or a positive number.

[Claim 2] The pattern formation approach characterized by developing a resist layer at the same time an alkali water solution removes an acid-resisting membrane layer after forming an acid-resisting membrane layer and exposing the above-mentioned resist layer by dissolving in water and applying an antireflection-film ingredient according to claim 1 on the photoresist film.

[Claim 3] The pattern formation approach characterized by forwater removing an acid-resisting membrane layer after forming an acid-resisting membrane layer and exposing the above-mentioned resist layer by dissolving in water and applying an antireflection-film ingredient according to claim 1 on the photoresist film, and subsequently removing a resist layer with an alkali water solution.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] in manufacture of a semiconductor integrated circuit etc. , especially this invention prevent lowering of the pattern dimensional accuracy produce in order that the laminating of the acid resisting membrane layer may be carry out and exposure light and the reflected light from a substrate may interfere within a photoresist layer on a photoresist layer on the occasion of the photoresist layer formation use at the time of the pattern formation of photolithography , and degradation of the resist pattern configuration by deactivation of the acid in a photoresist layer front face , and relate to the antireflection film ingredient and the resist pattern formation approach of make micro processing possible .

[0002]

[Description of the Prior Art] as the light source of recent years and far ultraviolet rays -- high -- although the technique of using a brightness KrF excimer laser attracts attention, when a photoresist layer with high transparency is used, the interferential action of incident light and the reflected light from a substrate arises. When irregularity is especially in a substrate, since the thickness of a resist layer changes a lot in a level difference part, it is influenced by light of interference, and the dimensional accuracy of a resist layer falls, and it stops being able to carry out pattern processing at exact size. Moreover, the dimensional accuracy of the alignment mark for doubling exposure also fell, and the problem of leading to lowering of doubling precision was also produced.

[0003] Furthermore, if the case where it is a positive-resist ingredient when the neglect time amount from exposure to PEB (Post Exposure Bake) becomes long is taken for an example when a chemistry magnification mold resist ingredient performs far ultraviolet rays, an electron ray, and X ray lithography, when pattern formation is carried out, a line pattern will become T-top configuration, namely, the problem [referred to as PED (Post Exposure Deley)] that the pattern upper part becomes thick will produce it. This is considered for the solubility of a resist layer front face to fall, and makes dimension control at a lithography process difficult. [W. which the problem of spoiling a dimension controllability even if it faces substrate processing using dry etching had produced Hinsberg et al., J.Photopolym.Sci.Technol., 6 (4), 535-546(1993)./T.Kumada et the 1994 spring Japan Society of Applied Physics related rehearsal [besides al., J.Photopolym.Sci.Technol., and 6(4)571-574(1993). / Hatanaka] collection, p567, 29p, and MB-2 reference --] .

[0004] ARCOR which forms an antireflection film in the resist upper layer that this problem should be solved -- various approaches are proposed as law (JP,62-62520,A, No. 62521 official report, etc.).

[0005] However, in the case of JP,62-62520,A, since the solubility over an organic solvent is low, a perfluoroalkyl compound must be diluted with the diluent of fluorine systems, such as chlorofluocarbon, and in case it removes the antireflection film containing the above-mentioned perfluoroalkyl compound, in order to use chlorofluocarbon etc. for it again, it has a problem from a viewpoint of environmental protection. Furthermore, it is industrially uneconomical, in order for a routing counter to increase and to use a very expensive solvent.

[0006] Moreover, since the refractive index is not low compared with the above-mentioned perfluoroalkyl compound, compared with a resist monolayer, only 2/3 can stop the amount of fluctuation of a pattern dimension, and the polysaccharide used as an antireflection film ingredient cannot be satisfied with the case of JP,62-62521,A of the amount.

[0007] furthermore, in the case of JP,6-118630,A, since the refractive index be low, if a chip, and the water-soluble inorganic acid currently moreover mention as an example of a proton generating matter and an organic acid with small molecular weight be add to the function as an antireflection film ingredient use for a chemistry magnification mold resist ingredient 10% of the weight or more among solid content like the fault of above-mentioned JP,62-62521,A, degradation of a pattern profile depend superfluously [supply of an acid] will take place. Moreover, when an ammonium weak acid salt is used as proton generating matter, the problem of Above PED cannot be solved.

[0008] Moreover, in JP,6-148896,A, since it is not the thing that solves the problem of PED of a chemistry magnification mold resist ingredient but a polyvinyl-pyrrolidone homopolymer, and there is no unit which has hydrophobicity, the membrane formation nature on the resist film is bad, and has the fault that a refractive index is also high.

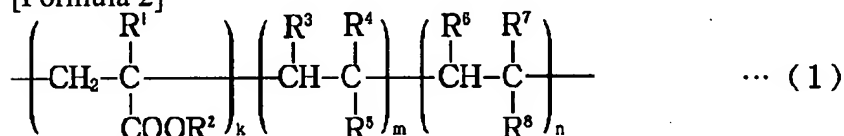
[0009] It is detailed, dimensional accuracy and doubling precision are high, and simple, it was made in view of the above-mentioned situation, and excels in membrane formation nature, productivity is high and forms a resist pattern with sufficient repeatability, it is cheap and this invention aims at offering an antireflection film ingredient safe for an environment, and the pattern formation approach.

[0010]

[The means for solving a technical problem and the gestalt of implementation of invention] By using together the fluororesin and the amine salt of a fluorine content organic acid which can dissolve in water easily and are shown by the following general formula (1) of a low refractive index not using a solvent like chlorofluorocarbon as a result of inquiring wholeheartedly, in order that this invention person may attain the above-mentioned object While giving the outstanding membrane formation nature, the knowledge of reducing the reflected light in a resist layer front face without loss of incident light, and being able to hold down the amount of fluctuation of the pattern dimension by optical multiplex interference in a resist layer to 1/2 or less compared with a resist monolayer was carried out.

[0011]

[Formula 2]



however, the inside R1 of a formula -- a hydrogen atom or a methyl group, and R2 -(CH2) a(CF2) bX or -CR nine R10R11, and R3 -- a hydrogen atom -- A methyl group or a carboxyl group, and R4 A hydrogen atom, a methyl group, a carboxyl group, or -CH2COOH, R5 A carboxyl group, a sulfonic group, -C(=O) YR12COOH, or -C(=O) YR12SO3H, A hydrogen atom, a methyl group or -COONR 13R14R15R16, and R7 R6 A hydrogen atom, A methyl group, - COONR 13R14R15R16 -CH2COONR 13R14R15R16 and R8 Or -COONR 13R14R15R16, -SO3NR 13R14R15R16, -C(=O) YR12COONR 13R14R15R16, or -C(=O) YR12SO3NR 13R14R15R16, A hydrogen atom, a fluorine atom or a trifluoromethyl radical, and at least 2 of R9-R11 R9-R11 A fluorine atom or a trifluoromethyl radical, The straight chain of carbon numbers 1-6 or the alkylene group of the letter of branching, and R13-R16 R12 A hydrogen atom, The alkyl group or alkyl group fluoride of the straight chain of carbon numbers 1-8, or the letter of branching, X -- a hydrogen atom or a fluorine atom, and Y -O- or -NH-, -, a are [the integer of 1-8, and k and the ratio of (m+n) of 0-2b] k:(m+n)=1:9-9:1, and k is a positive number, m and n0, or a positive number.

[0012] That is, in case the antireflection film which used the fluororesin of a general formula (1) is formed on a resist layer, in a resin independent water solution, membrane formation nature may be inferior. If the content of the fluorine content unit especially contained in fluororesin exceeds 50-mol %,

striae SHON will occur and degradation of membrane formation nature will become remarkable. On the other hand, while reducing the refractive index of an antireflection film ingredient by using together the amine salt of a fluorine content organic acid, the membrane formation nature of an antireflection film is raised. In this case, if a fluorine content organic acid is used as an additive, an acid will be spread in a resist layer. A resist film front face dissolves with the resist ingredient which has especially an acid instability radical. Although film decrease of the resist film becomes large and is not desirable, when the amine salt of a fluorine content organic acid is used, since the acid is neutralized, the effectiveness of not dissolving a resist film front face and raising membrane formation nature also becomes large compared with a fluorine content organic acid.

[0013] Here, in the amine salt of the fluoro-resin of the above-mentioned general formula (1), if the salt of the amine which has especially alkyl group fluoride is used, while being able to enlarge the fluorine atom content in resin and being able to make it fall one layer of refractive-index nearby, a refractive index can be further lowered by adding the amine salt of a fluorine content organic acid to the fluoro-resin of the above-mentioned general formula (1). Moreover, the trap of the basic compound in air can be carried out by the sulfonic group of the fluoro-resin shown by the above-mentioned general formula (1), and the problem of PED can be solved. Furthermore, the amine salt of a fluorine content organic acid can lower the refractive index of a protective coat, without carrying out deactivation of the acid of a resist layer front face by combining with the fluoro-resin which has a strong acid radical like a sulfonic group. And these are useful also as a protective coat of the chemistry magnification mold resist upper layer which is hard to diffuse in a resist layer since molecular weight is large, and can solve the problem of degradation of the resist layer of a pattern profile.

[0014] That is, since the reflection factor of light can be substantially reduced if it becomes a low refractive index (refractive index; about 1.50 or less) and this film is made into the upper layer of a resist layer when film formation is carried out using the antireflection film ingredient of this invention, when the dimensional accuracy of a resist image can be raised, the amount of fluctuation of the pattern dimension by optical multiplex interference in a resist layer can be held down to 1/2 or less compared with a resist monolayer.

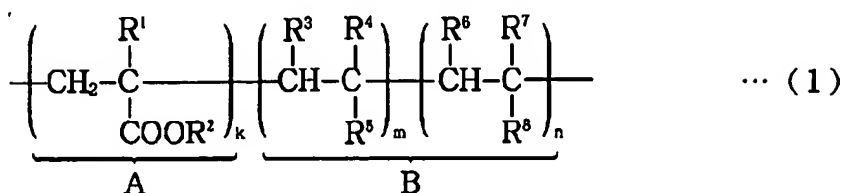
[0015] Moreover, general fluoro-resin has water repellence, and to dissolving only in a special solvent like chlorofluorocarbon, since the fluoro-resin shown by the above-mentioned formula (1) has a carboxyl group, a sulfonic group, or a hydrophilic radical called these amine salts, it dissolves it in water easily. Therefore, insurance and cheap water can perform antireflection film formation easily, and even if it moreover faces clearance of an antireflection film, it can carry out easily and thoroughly using water. Furthermore, since the resin shown by the above-mentioned formula (1) dissolves also in the alkali water solution used for the development of a resist layer easily, it can perform simultaneously the development of a resist layer and the clearance of an antireflection film layer by the alkali water solution, and can shorten a pattern formation process.

[0016] Therefore, by carrying out the laminating of this on a photoresist layer, and forming an acid-resisting membrane layer, degradation of the resist pattern configuration by deactivation of the acid in a photoresist layer front face can be prevented, moreover INTAMIKISHINGU in a resist layer-antireflection-film interface is not started, and a process process is also satisfactory and, as for the antireflection-film ingredient of this invention, safe for an environment.

[0017] Hereafter, it is formed per this invention and also on the photoresist layer which formed this invention on the substrate when explained in detail, and the water shown by the following general formula (1) is provided with the antireflection film ingredient which uses the amine salt of meltable fluoro-resin and a fluorine content organic acid as a principal component in the antireflection film ingredient which forms the transparent antireflection film removed with a solvent after exposure.

[0018]

[Formula 3]



however, the inside R1 of a formula -- a hydrogen atom or a methyl group, and R2 -(CH2) a(CF2) bX or -CR nine R10R11, and R3 -- a hydrogen atom -- A methyl group or a carboxyl group, and R4 A hydrogen atom, a methyl group, a carboxyl group, or -CH2COOH, R5 A carboxyl group, a sulfonic group, -C(=O) YR12COOH, or -C(=O) YR12SO3H, A hydrogen atom, a methyl group or -COONR 13R14R15R16, and R7 R6 A hydrogen atom, A methyl group, - COONR 13R14R15R16 -CH2COONR 13R14R15R16 and R8 Or -COONR 13R14R15R16, -SO3NR 13R14R15R16, -C(=O) YR12COONR 13R14R15R16, or -C(=O) YR12SO3NR 13R14R15R16, R9-R11 are a hydrogen atom, a fluorine atom, or a trifluoromethyl radical. As for a fluorine atom or a trifluoromethyl radical, and R12, the straight chain of carbon numbers 1-6 or the alkylene group of the letter of branching, and R13-R16 are [at least two of R9-R11] the alkyl group or alkyl group fluoride of the straight chain of a hydrogen atom and carbon numbers 1-8, or the letter of branching. Moreover, X is a hydrogen atom or a fluorine atom, Y is -O- or -NH-, a is [the integer of 1-8, and k and the ratio of (m+n) of 0-2b] k:(m+n)=1:9-9:1, and k is a positive number, m and n0, or a positive number.

[0019] The fluororesin of the above-mentioned formula (1) becomes the water and the alkali water solution of a fluorine atom content unit and Above B in which the refractive index of Above A is reduced from the hydrophilic unit for making it meltable, and the following are mentioned as an example of A unit monomer.

CH2=CHCOOCH2CF3, CH2=CHCOOCH2 2H, CH2=CHCOOCH2 (CF2) 2F, CH2=CHCOOCH (CF2) (CF3) 2, CH2=CHCOOCH2(CF2)4H, CH2=CHCOOCH2CH2(CF2)4F, CH2=CHCOOCH2CH2 (CF2)8F, CH2=C(CH3) COOCH2CH2(CF2)8F[0020] The hydrophilic unit of B consists of a unit

which has the monomer unit which has acidic groups, such as a carboxyl group and a sulfonic group, and these amines salt. Moreover, the thing with a fluoride alkylamine salt serves as both the role with which a refractive index is reduced, and the role for making it meltable in water and an alkali water solution by Above B. As an example of m unit of B unit monomer, an acrylic acid, a methacrylic acid, an itaconic acid, a maleic acid, a vinyl sulfonic acid, 2-acrylamido-2-methyl propane sulfonic acid, etc. are mentioned. Moreover, as an example of n unit of B unit monomer, an ammonium salt [of m unit monomer], ethylamine salt, diethylamine salt, triethylamine salt, propylamine salt, butylamine salt, 1H, and 1H-pentafluoro propylamine salt, a perfluoro triethylamine salt, etc. are mentioned. k which shows the abundance ratio of a fluorine atom content unit (A) and a hydrophilic unit (B), and the ratio of (m+n) are 1:9-9:1 in a mole ratio.

[0021] As for the refractive index of the fluororesin of the above-mentioned formula (1), it is desirable with 248nm wavelength light that it is [or more 1] 1.5 or less here, it is desirable that the weight of the fluorine atom occupied to fluororesin for that purpose is 30 % of the weight or more, and since 30 - 60 % of the weight is desirable for becoming still more nearly meltable in water and an alkali water solution, it is desirable to adjust k and a ratio with (m+n) so that it may become this range.

[0022] Moreover, since a hydrophobic property becomes strong so that the carbon number of the fluorine atom content unit A and the number of fluorines increase, it is desirable for (m+n) to be large for becoming meltable in water and an alkali water solution. For example, by the case where R4 is a tetrafluoro propyl group, k:(m+n)=7:3-5:5 become the optimal by the case where R4 is a heptadeca fluoro decyl group, to the range of k:(m+n)=8:2-6:4 being the optimal in respect of both solubility and a refractive index. A refractive index low enough may not be obtained with in any case, it becoming insoluble in water and an alkali water solution, or refractory, if the ratio of k exceeds the above-mentioned range, and the ratio of k being under the above-mentioned range. Moreover, if the hydrophilic unit B is a fluoride alkylamine salt, even if the ratio of k is lower than the above-mentioned presentation, since it becomes large, the antireflection film ingredient of a low refractive index tends to

obtain the fluorine content contained in an antireflection film ingredient.

[0023] The hydrophilic unit B of the above-mentioned formula (1) consists of a unit which has an acidic group, and a unit which has an amine salt, as mentioned above, but since there is a possibility of carrying out deactivation of the acid on the front face of a resist when an amine salt is an amine salt of weak acid like a carboxylic acid here, having simultaneously the unit which has an acidic group, or adding a fluorine content organic acid is recommended. In a mole ratio, the abundance ratios of m and n at this time are 1:9-9:1, and are 5:5-9:1 more preferably.

[0024] On the other hand, since deactivation of the acid on the front face of a resist cannot happen easily when an amine salt is an amine salt of strong acid like a sulfonic acid, it is not necessary to necessarily introduce the unit which has an acidic group.

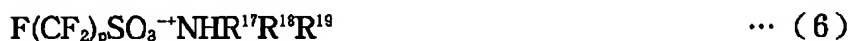
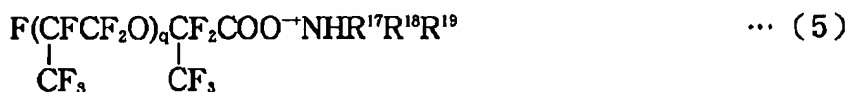
[0025] The fluoro-resin of the formula (1) which is the principal component of the antireflection-film ingredient of this invention is quantitatively [easily and] compoundable by making the resin obtained by the approach of the radical polymerization of a fluorine atom content vinyl monomer and the vinyl monomer which has a carboxyl group and a sulfonic group etc., and a corresponding amine react. Moreover, it is compoundable with copolymerization of the amine salt of a monomer and fluorine atom content vinyl monomer which the vinyl monomers which have a carboxyl group and a sulfonic group, and those amines were made to react, and were obtained.

[0026] If it is desirable that the number average molecular weight is 1,000-1,000,000 as for the fluoro-resin of the above-mentioned formula (1) and it carries out to especially 2,000-20,000, it is more suitable. Membrane formation nature may worsen that number average molecular weight is less than 1,000, if 1,000,000 is exceeded, the solubility of fluoro-resin may fall, and it may become difficult to obtain meltable fluoro-resin in water.

[0027] In this invention, as mentioned above, the amine salt of a fluorine content organic acid is blended further. The following can be mentioned as an amine salt of this organic acid.

[0028]

[Formula 4]



(The integer of 4-15 and q of p are the integers of 1-10 among a formula.) R¹⁷-R¹⁹ are a hydrogen atom or the alkyl group of carbon numbers 1-8, for example, a methyl group, an ethyl group, and its an isopropanol radical are desirable. Moreover, even if R¹⁷-R¹⁹ are mutually the same, they may differ.

[0029] in order that the loadings of solid content which consist of an amine salt of fluoro-resin and a fluorine content organic acid may set the thickness of a water-soluble layer as 300-3,000Å (0.03-0.3 micrometers) in this invention -- the whole -- 2 - 15 % of the weight is especially desirable one to 30% of the weight. It becomes [if the loadings of solid content are not filled to 1% of the weight, thickness will become thinner than 300Å, the acid-resisting effectiveness and a PED protective effect may not no

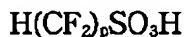
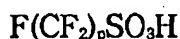
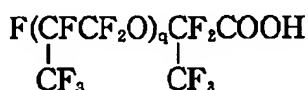
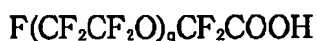
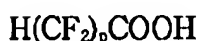
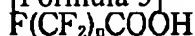
longer be acquired, if 30 % of the weight is exceeded, thickness will become thicker than 3,000A, and / the burden at the time of an exfoliation process] large and is not desirable.

[0030] Furthermore, the antireflection film ingredient of this invention is a mixed water solution which it comes to contain 20 to 50% of the weight ten to 60% of the weight still more preferably preferably five to .70% of the weight among solid content about the amine salt of a fluorine content organic acid 40 to 90% of the weight preferably 30 to 95% of the weight among solid content in fluororesin. If fluororesin is not filled to 30% of the weight, compatibility and membrane formation nature may worsen.

[0031] In addition, a fluorine content organic acid as shown in the following type if needed can also be blended with the antireflection film ingredient of this invention.

[0032]

[Formula 5]



(p and q show the same semantics as the above among a formula.)

[0033] Although the antireflection-film ingredient of this invention functions as a protective coat as antireflection film of a chemistry magnification mold resist ingredient, it can be used also as antireflection film of a general-purpose resist layer using a diazo naphthoquinone compound etc.

[0034] In order to form the resist pattern using the antireflection-film ingredient of this invention, the lithography process which can adopt a well-known approach, for example, is shown in drawing 1 can perform. First, a photoresist layer 2 is formed by the approach of a spin coat etc. on the substrates 1, such as a silicon wafer. On this photoresist layer 2, apply the antireflection film ingredient of this invention by the approach of a spin coat etc., and the antireflection film layer 3 is formed. Ultraviolet rays with a wavelength of 190-500nm or an excimer laser 4 is exposed in a desired pattern configuration by cutback projection at the antireflection film layer 3. That is, A part can be exposed in drawing 1 (c), and a resist pattern 5 can be formed by the approach of performing simultaneously clearance and development of an acid-resisting membrane layer using an alkali developer. In addition, after exposure, since the process of resist pattern formation becomes complicated, this approach has a method more desirable [after removing the antireflection film layer 3 using water, negatives can also be developed using an alkali water solution, but] of performing clearance and development of an antireflection film simultaneously, using an alkali water solution as the resist pattern formation approach.

[0035] In this case, it is desirable the thickness of 300-2000A and to form especially the antireflection film layer 3 in the thickness of 420A and about 1270A in the case of 248nm exposure light.

[0036] Since the positive-resist ingredient was used as a photoresist layer 2 in the example shown in drawing 1 , B part remains as a resist pattern, but if the contrast threshold of predetermined level is shown to the light of predetermined wavelength as a photoresist ingredient, both a positive type and a

negative mold can be used.

[0037] If here explains the light-scattering reduction effectiveness of the antireflection film by the antireflection film ingredient of this invention with reference to drawing 2 and 3, as shown in drawing 2, only by forming the resist layer 2 in a substrate 1 While the echo (Ir1) with incident light Io remarkable at an air-resist layer interface takes place and the amount of incident light loses Since it is repeated that the light which entered in the resist layer 2 reflects by the resist layer-substrate interface (Ir2), and this reflected light Ir2 reflects again by the resist layer-air interface (Ir3), an optical multiplex interference arises in a resist layer.

[0038] On the other hand, as shown in drawing 3, the reflected light Ir4 in the air-antireflection film layer interface of incident light Io and the reflected light Ir5 in an antireflection film layer-resist interface can be reduced by forming the antireflection film layer 3 of this invention on the resist layer 2. Thus, since the reflected lights Ir4 and Ir5 can be reduced, loss of the amount of incident light decreases, and since the reflected lights Ir6 and Ir7 have the reverse phase of light, it weakens each other, and an optical multiplex interference within the resist layer 2 is controlled.

[0039] That is, the reflection factor (gain) of this acid resisting is reduced, so that it will bring refractive-index n' of an antireflection film close to \sqrt{n} and that thickness will be close brought by odd times $\lambda/4n'$ from the principle of acid resisting, if wavelength of n and exposure light is set to λ for the refractive index to the exposure light of a resist.

[0040] If it follows, for example, the refractive index in the wavelength same as a chemistry magnification resist ingredient as the ingredient of the polyhydroxy styrene system whose refractive index with a wavelength of 248nm is about 1.78 carries out pattern formation with a KrF excimer laser with a wavelength of 248nm using the antireflection film ingredient of this invention which is about 1.43, odd about 430A times will become the optimal thickness of an antireflection film. In this case, the reduction effectiveness of the above-mentioned reflected light and optical multiplex cross protection are demonstrated effectively.

[0041]

[Effect of the Invention] The antireflection-film ingredient of this invention is useful as a protective coat ingredient as an ingredient which forms the antireflection film which is excellent in membrane formation nature, and reduces the reflected light in a resist layer front face without loss of incident light, and reduces the amount of fluctuation of the pattern dimension by optical multiplex interference in a resist layer.

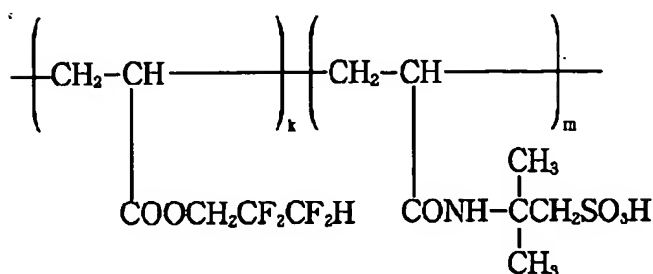
[0042]

[Example] Although a synthetic example, an example, and the example of a comparison are shown and this invention is explained concretely hereafter, this invention is not restricted to the following example.

[0043] [Synthetic example 1] Methanol 146g was added as acrylic-acids 2, 2, and 3 and 3-tetrafluoro propyl 27.9g, 20.7g of 2-acrylamide-2-methyl-1-propane sulfonic acids, and a solvent, and 1.46g of tert-butyl peroxi-2-ethylhexanoate was added to the synthetic autoclave of Pori (acrylic acids 2, 2, and 3, 3-tetrafluoro propyl-co-2-acrylamide-2-methyl-1-propane sulfonic acid) (resin 1) as a catalyst. The system was sealed after deaerating by carrying out bubbling of the desiccation nitrogen, stirring with for [sufficient] about 15 minutes. Stirring well, the system was heated at 80 degrees C and the polymerization was performed for 6 to 7 hours. Next, after fully cooling the system of reaction and suspending a polymerization, the obtained reaction solution was poured in into the hexane and resin was isolated. Furthermore, when reprecipitation and washing were repeated and refined, Pori (acrylic-acids 2, 2, and 3, 3-tetrafluoro propyl-co-2-acrylamide-2-methyl-1-propane sulfonic acid) 48.3g was obtained. In addition, the presentation of the obtained resin was checked by 1 H-NMR and elemental analysis. The presentation ratio of acrylic acids 2, 2, and 3, 3-tetrafluoro propyl, and a 2-acrylamide-2-methyl-1-propane sulfonic acid was k:m=6:4 about.

[0044]

[Formula 6]

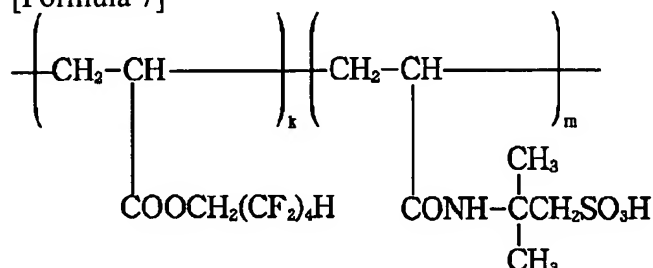


樹脂 1

[0045] [Synthetic example 2] as a monomer which carries out a synthetic polymerization in Pori (acrylic acids 1H and 1H, 5H-octafluoropentyl-co-2-acrylamide-2-methyl-1-propane sulfonic acid) (resin 2) Copolymerization is performed like the synthetic example 1 except using acrylic-acids 1H and 1H and 5H-octafluoropentyl 19.1g instead of acrylic acids 2, 2, and 3 and 3-tetrafluoro propyl. Pori (acrylic-acids 1H and 1H, 5H-octafluoropentyl-co-2-acrylamide-2-methyl-1-propane sulfonic acid) 39.5g was compounded. The presentation ratio of acrylic acids 1H and 1H, 5H-octafluoropentyl, and a 2-acrylamide-2-methyl-1-propane sulfonic acid was k:m=4:6 about.

[0046]

[Formula 7]

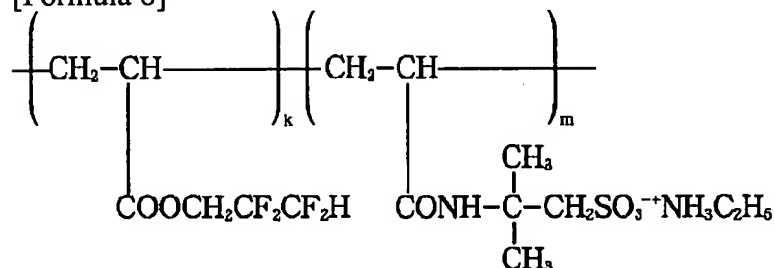


樹脂 2

[0047] [Synthetic example 3] 48.3g and ethylamine 13.5g of resin 1 compounded in the example 1 of synthetic composition of Pori (acrylic acids 2, 2, and 3, 3-tetrafluoro propyl-co-2-acrylamide-2-methyl-1-propane sulfonic-acid ethylammonium) (resin 3) Inside of ethanol, After making it react at 50 degrees C for 2 hours, reduced pressure distilling off of ethanol and the superfluous ethylamine was carried out, and Pori (acrylic-acids 2, 2, and 3, 3-tetrafluoro propyl-co-2-acrylamide-2-methyl-1-propane sulfonic-acid ethylammonium) 52.8g was obtained. The presentation of the obtained resin was checked by 1 H-NMR and elemental analysis. The presentation ratio of acrylic acids 2, 2, and 3, 3-tetrafluoro propyl, and 2-acrylamide-2-methyl-1-propane sulfonic-acid ethylammonium was k:m=6:4 about.

[0048]

[Formula 8]

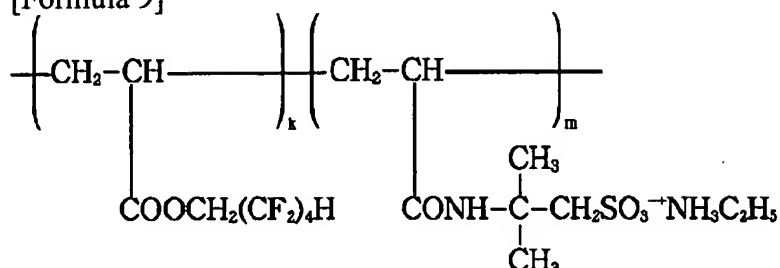


樹脂 3

[0049] [Synthetic example 4] 39.5g and ethylamine of resin 2 which were compounded in the example 2 of synthetic composition of Pori (acrylic acids 1H and 1H, 5H-octafluoropentyl-co-2-acrylamide-2-methyl-1-propane sulfonic-acid ethylammonium) (resin 4) It was made to react by the same approach as the synthetic example 4, and Pori (acrylic-acids 1H and 1H, 5H-octafluoropentyl-co-2-acrylamide-2-methyl-1-propane sulfonic-acid ethylammonium) 44.0g was obtained. The presentation ratio of acrylic acids 1H and 1H, 5H-octafluoropentyl, and 2-acrylamide-2-methyl-1-propane sulfonic-acid ethylammonium was k:m=4:6 about.

[0050]

[Formula 9]

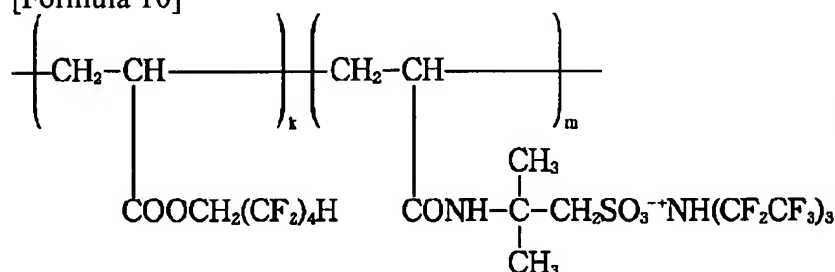


樹脂 4

[0051] [Synthetic example 5] Pori (1H 1H of acrylic acids) Synthetic Pori of 5H-octafluoropentyl-co-2-acrylamide-2-methyl-1-propane sulfonic-acid perfluoro triethyl ammonium (resin 5) (1H of acrylic acids) 1H, and 23.1g (presentation ratio 3:7) of 5H-octafluoropentyl-co-2-acrylamide-2-methyl-1-propane sulfonic acids and perfluoro triethylamine are made to react by the same approach as the synthetic example 4. Pori (acrylic-acids 1H and 1H, 5H-octafluoropentyl-co-2-acrylamide-2-methyl-1-propane sulfonic-acid perfluoro triethyl ammonium) 48.9g was obtained. The presentation ratio of acrylic acids 1H and 1H, 5H-octafluoropentyl, and 2-acrylamide-2-methyl-1-propane sulfonic-acid perfluoro triethyl ammonium was k:m=3:7 about.

[0052]

[Formula 10]

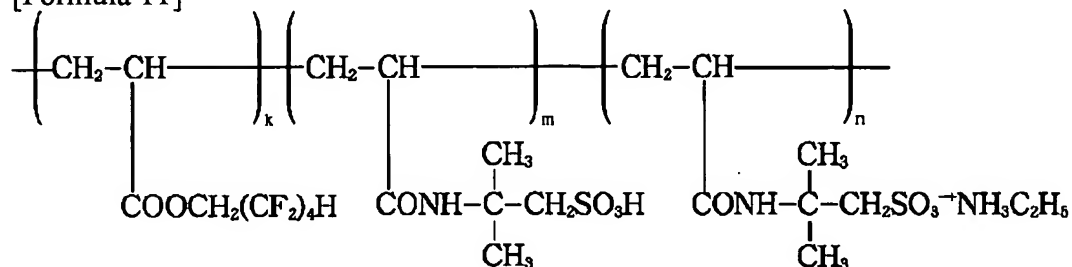


樹脂 5

[0053] [Synthetic example 6] Pori (1H 1H of acrylic acids) 39.5g of the resin 2 compounded in the example 2 of synthetic composition of 5H-octafluoropentyl-co-2-acrylamido-2-methyl-propane-sulfonic-acid-co-2-acrylamide-2-methyl-1-propane sulfonic-acid ethylammonium (resin 6) After making ethylamine 2.25g react by the same approach as the synthetic example 4, the obtained reaction mixture was poured in into the hexane and resin was isolated. Furthermore, when reprecipitation and washing were repeated and refined, Pori (acrylic-acids 1H and 1H, 5H-octafluoropentyl-co-2-acrylamide-2-methyl-1-propane sulfonic-acid-co-2-acrylamide-2-methyl-1-propane sulfonic-acid ethylammonium) 41.7g was obtained. The presentation ratio of a monomer unit was k:m:n=4:3:3 about.

[0054]

[Formula 11]



樹脂 6

[0055] [Example 1] According to the lithography process which shows FC-93 (the product made from Sumitomo 3M, perfluoro octane sulfonic-acid ammonium) to drawing 1 for resin 1 as an antireflection

film ingredient using 5.0% of the weight of a water solution to 30% of the weight of solid content, the resist pattern was formed to 70 % of the weight.

[0056] First, prebaking (100 degrees C, 90 seconds) behind a spin coat was performed for SEPR-X04 (the Shin-Etsu Chemical Co., Ltd. make, positive resist) to the substrate 1 which consists of a silicon wafer etc., and the resist layer 2 was formed (drawing 1 (a)). Next, when the spin coat of the above-mentioned antireflection film ingredient was carried out on the resist layer 2, 420A of thickness and the 1270A antireflection film layer 3 were formed good (drawing 1 (b)), and exposed the 248nm KrF excimer laser light 4 selectively into A part by cutback projection (drawing 1 (c)). Heat treatment was performed after carrying out predetermined time neglect of this wafer (90-degree-C 90 seconds). Next, clearance and development of an acid-resisting membrane layer were simultaneously performed using the alkali developer, and the resist pattern 5 was formed (drawing 1 (d)).

[0057] The obtained resist pattern was able to reduce the 0.3-micrometer line dimension variation accompanying fluctuation of resist thickness which had about 900A to about 300A with photoresist monolayer lithography, without starting INTAMIKISHINGU in an interface with a photoresist. Moreover, the resist pattern configuration was good irrespective of the time amount from exposure to PEB, and degradation of the resist pattern configuration of formation of a surface refractory layer was not observed.

[0058] [Example 2] As an antireflection film ingredient, in resin 2, as a result of performing [EF-101 (MITSUBISHI MATERIALS Make, perfluoro octane sulfonic acid)] resist pattern formation for FC-93 by the same approach as an example 1 to 5 % of the weight 65% of the weight using 5.0% of the weight of a water solution to 30% of the weight of solid content, the same result was obtained.

[0059] [Example 3] As an antireflection film ingredient, in the 9H-hexa deca fluoro nonoic acid ethylammonium which resin 2 was made to react 50% of the weight, and compounded C-5800 (made in Daikin Fine chemical Lab, 9H-hexafluoro nonoic acid), and ethylamine, as a result of performing resist pattern formation by the same approach as an example 1 using 5.0% of the weight of a water solution to 50% of the weight of solid content, the same result was obtained.

[0060] [Example 4] As an antireflection-film ingredient, in resin 3, 50% of the weight, as a result of performing resist pattern formation by the same approach as an example 1 using 5.0% of the weight of a water solution to 50% of the weight of solid content, the same result was obtained [ethylammonium / 9H-hexa deca fluoro nonoic acid].

[0061] [Example 5] As an antireflection-film ingredient, in resin 4, 50% of the weight, as a result of performing resist pattern formation by the same approach as an example 4 using 5.0% of the weight of a water solution to 50% of the weight of solid content, the same result was obtained [ethylammonium / 9H-hexa deca fluoro nonoic acid].

[0062] [Example 6] As an antireflection-film ingredient, in resin 5, 50% of the weight, as a result of performing resist pattern formation by the same approach as an example 5 using 5.0% of the weight of a water solution to 50% of the weight of solid content, the same result was obtained [ethylammonium / 9H-hexa deca fluoro nonoic acid].

[0063] [Example 7] As an antireflection-film ingredient, in resin 6, 50% of the weight, as a result of performing resist pattern formation by the same approach as an example 5 using 5.0% of the weight of a water solution to 50% of the weight of solid content, the same result was obtained [ethylammonium / 9H-hexa deca fluoro nonoic acid].

[0064] [Example 1 of a comparison] Resist pattern formation was performed by the same approach as an example 1, using 3.0% water solution of polyacrylic acid (Mw=6000) as an antireflection film ingredient.

[0065] The obtained resist pattern was good irrespective of the time amount from exposure to PEB, without starting INTAMIKISHINGU in an interface with a photoresist, and degradation of the resist pattern configuration of formation of a surface refractory layer was not observed. However, in photoresist monolayer lithography, the dimension variation accompanying fluctuation of resist thickness which had about 900A remained as it was, and was not able to be reduced.

[0066] [Example 2 of a comparison] Resist pattern formation was performed by the same approach as an

example 1 as an antireflection film ingredient using AquaTAR (Hoechst A.G. make) containing a polyacrylic acid homopolymer and fluoro alkyl ammonium salt.

[0067] The obtained resist pattern was able to reduce the dimension variation accompanying fluctuation of resist thickness which had about 900A to about 400A with photoresist monolayer lithography, without starting INTAMIKISHINGU in an interface with a photoresist. However, the resist pattern configuration turned into T-top configuration, and the surface refractory layer became large as the time amount from exposure to PEB was extended.

[0068] [Example 3 of a comparison] As a result of forming an antireflection film by the same approach as an example 1, using the 3.0-% of the weight water solution of resin 2 as an antireflection film ingredient, striae SHON occurred and degradation of membrane formation nature was remarkable.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is a sectional view explaining the lithography process using the antireflection film ingredient of this invention.

[Drawing 2] It is a sectional view explaining the light-scattering condition of the resist layer which does not form the antireflection film.

[Drawing 3] It is a sectional view explaining the light-scattering condition of the resist layer using the antireflection-film ingredient of this invention.

[Description of Notations]

1 Substrate

2 Photoresist Layer

3 Antireflection Film Layer

[Translation done.]